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Palladium Complexes Comprising C(4)-bound Diimidazolylidene Carbenes

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Abstract

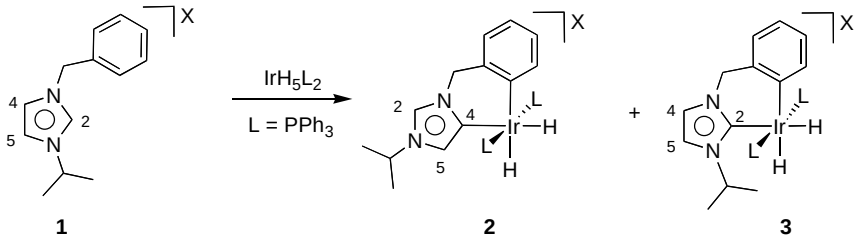
Imidazolium-derived palladium dicarbene complexes have been synthesized which feature either normal C(2) carbene bonding or abnormal C(4) bonding. Comparison of the reactivity of these complexes, in particular towards Lewis acids (H^+, Ag^+), indicate consistently that C(4)-bound carbenes are stronger donors than their C(2)-bound analogs. As a consequence of this electronic impact, palladium complexes comprising C(4)-bound dicarbene ligands were found to be efficient catalysts for olefin hydrogenation under mild conditions.

Keywords

N-heterocyclic carbenes, abnormal bonding, palladium, catalytic alkene hydrogenation

Introduction

In the last few years, N-heterocyclic carbenes (NHCs) have emerged as versatile ligands in transition-metal chemistry. They are strong neutral donors and thus powerful ligands for catalysis, and have been successfully applied in C–C coupling reactions,[1] olefin methathesis,[2] hydroformylation,[3] polymerization reactions,[4] and C–H bond activation.[5] NHC ligands usually coordinate to the metal center at their C(2) position. Recently, abnormal C(4)-bonding (Scheme 1) has been discorvered as a new NHC coordination mode. Such C(4)-bound carbenes represent a new type of ligand for transition metals. The reduced heteroatom stabilization may induce stronger donor properties, which will be advantageous for various catalytic applications.



Scheme 1. Synthesis of C(4)-bound carbene complexes with iridium polyhydrides.

Originally C(4)-bound carbene complexes have been synthesized by metallation of 2-pyridylimidazolium salt **1** with $[IrH_5(PPh_3)_2]$, which gave the abnormal complex **2** with the metal

bound to C(4) instead of the expected C(2)-bound complex **3** (Scheme 1).[6] The nature of the counter anion appeared to have a decisive influence on the binding mode.[7] Strongly coordinating anions such as Br^- form hydrogen bonds with the more acidic C(2)-bound proton, thus favoring a proton transfer mechanism and heterolytic C(2)–H cleavage. In contrast weakly coordinating anions such as BF_4^- facilitate C(4)–H oxidative addition. A similar anion influence has been observed upon palladation of bis(mesityl)imidazolium salts. In the presence of Cs_2CO_3, only the normal C(2)-bound complex **4** is formed, while in the absence of additives the mixed normal/abnormal complex **5** is obtained.

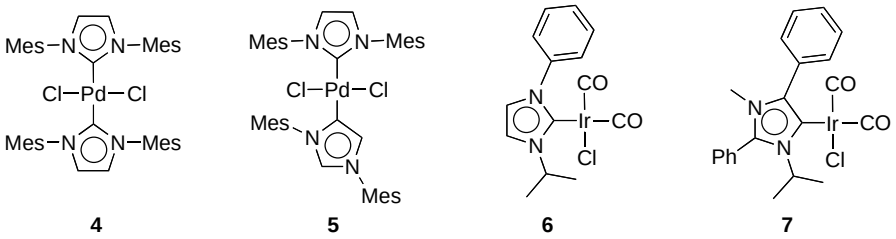


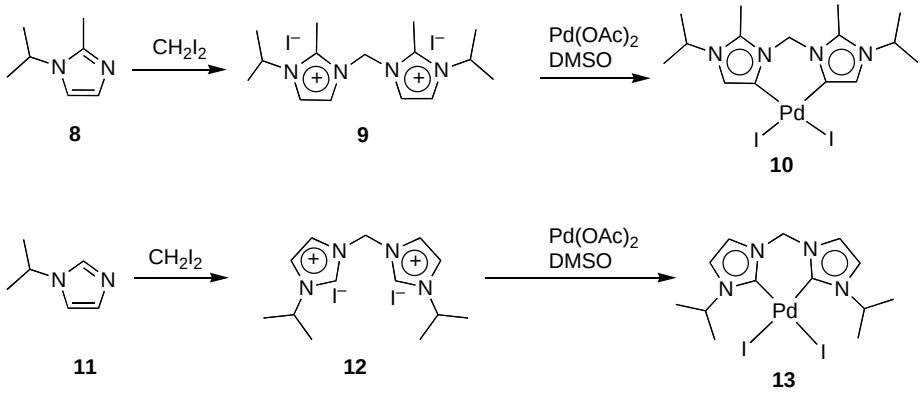
Figure 1. Normal and abnormal NHC complexes of palladium(II) and iridium(I).

A less anion-sensitive synthesis of C(4)-bound carbene complexes involves the protection of the C(2) position in the imidazolium precursor. Accordingly, the structurally very similar complexes **6** and **7** have been prepared in order to study the electronic impact of normal and abnormal carbenes (Figure 1).[8] Complex **7** shows much lower ν(CO) frequencies than complex **6**, indicating that the abnormal carbene in **7** is a stronger donor than its normal C(2)-bound analog in **6**. In addition complex **4** and its C(4)-bound analog **5** were tested in Suzuki and Heck reactions.[9] The mixed C(2)–C(4) bound biscarbene complex **5** shows significantly better catalytic activity than **4**. Apparently the bonding mode increases the catalytic performance of the metal center.

We are interested in further pursuing this approach, in particular for finding systems that allow for catalytic activation of less reactive bonds. In order to fully exploit the expected high *trans* effect of these abnormal carbenes, rigidly *cis* coordinating ligands are desirable. Our studies therefore focused on bidentate dicarbene ligands and their palladium complexes. Here we show that C(4)-bound carbenes are stronger donors than their C(2)–bound analogs. These properties have been successfully utilized for developing a new catalytic olefin hydrogenation process that operates under mild conditions.

Synthesis of complexes

The use of C–H bond activation as rational synthetic route for C(4)-metallation of imidazolium salts requires the functionalization of the C(2) position to prevent normal C(2) binding. Therefore the imidazole **8** with a methyl substituent at C(2) was chosen as starting material. It was readily converted into the diimidazolium salt **9** by using diiodomethane (Scheme 2). Metallation was successfully accomplished with $Pd(OAc)_2$ in DMSO, thus yielding the abnormal dicarbene complex **10** (Scheme 2).[10] A similar route starting from 2-H-isopropylimidazol **11** gave the complex **13** with carbene ligands bound normally via C(2).[11] Both complexes **10** and **13** were obtained in high yield and their structures were confirmed by spectroscopy and X-ray analysis.



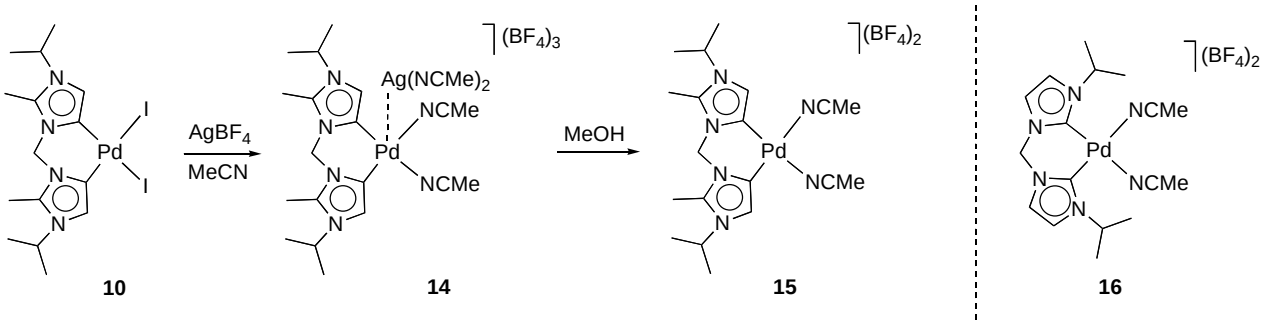
Scheme 2. Synthesis of C(2)- and C(4)-bound palladium complexes **10** and **13**.

Reactivity towards Lewis acids

In the presence of H_2SO_4, the C(4)-bound complex **10** dissociates rapidly to give a diimidazolium salt similar to **9**. In contrast the C(2)-bound analog **13** is stable under identical conditions for days, even upon heating. Obviously the palladium center is less acid-stable in abnormal complexes. The metal-bound carbon is a possible site of direct proton attack, since this position is not shielded by wingtip groups as in **13**. Alternatively proton-binding can occur initially at the palladium center, forming a Pd-hydrogen intermediate. Subsequent hydrogen migration to the metal-bound carbon with concomitant cleavage of the Pd–C bond also gives the diimidazolium salt. We were unable to detect any Pd–H intermediate by in situ ^{1}H NMR spectroscopy, but reactivity studies of complex **10** towards other Lewis acids supports such a metal-mediated pathway.

The abnormal complex **10** reacts with $AgBF_4$ to give the unexpected bimetallic complex **14** (Scheme 3).[10] Atomic absorption spectroscopy indicates the presence of equimolar quantities of silver and palladium in complex **14**. The structure was unequivocally confirmed by X-ray analysis and shows a remarkably short Pd···Ag contact of 2.8701(6) Å (Figure 2).[12] This supports a strong Pd–Ag bond in complex **14**. Hence this complex may represent a model for the postulated Lewis acid–Lewis base intermediate in the reaction of **10** with H^+ ions.

The silver-free bissolvento complex **15** is obtained by dissolving the silver adduct in MeOH or DMSO (Scheme 3). These solvents are nucleophilic enough to compete with the palladium center and hence promote the transfer of Ag^+ from palladium to a solvent oxygen site. In contrast to **10**, the normal dicarbene complex **13** gave directly the expected bissolvento complex **16** upon addition of $AgBF_4$ (Scheme 3).[11]



Scheme 3**.** Reactivity of **10** and **13** towards $AgBF_4$.

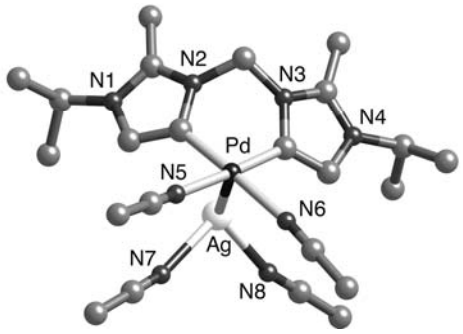


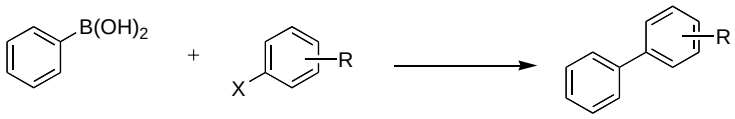
Figure 2. Molecular structure of the bimetallic species **14** displaying a short palladium-silver interaction.

Apparently, the palladium center in the abnormal carbene complex **10** is electron-rich enough to coordinate to a Lewis acid such as Ag^+. This suggests that the palladium is more nucleophilic in C(4)-bound carbene complexes than in C(2)-bound analogs, which may be due to the stronger donor ability of abnormal carbenes. Additionally, steric effects may also contribute to the observed reactivity differences. In the C(2)-bound complex **13** the Pd–C bond is shielded by the iso-propyl wingtip group, which may prevent coordination of Lewis acids to the metal center.

Current investigations in our laboratories on complexes that feature identical steric environments indicate however that steric effects are negligible and that, indeed, the reactivity differences are due to the electronic effects. This hypothesis was further verified by X-ray photoelectron spectroscopy (XPS). The 3d electron bonding energies at the palladium center in **10** are 0.6 eV lower than those in the C(2)-bound complex **13**. This difference implies a higher electron density at the metal center when bound to abnormal carbenes and supports the notion that C(4)-bound carbenes are stronger electron donors than their C(2)-bound analogs.

Catalysic applications

The impact of C(4)-bound carbene ligands has been exploited in catalysis, particularly in Suzuki cross-coupling and in alkene hydrogenation. Complexes **10** and **13** both catalyze the Suzuki cross-coupling of aryl bromides with phenyl boronic acid (Eq 1). For both complexes yields are acceptable but high catalyst loadings and long reaction times are required. Accordingly TONs and TOFs are very low.

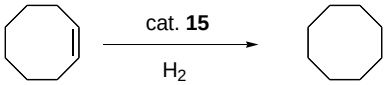


(1)

The limited activity of complexes **10** and **13** in cross-coupling reactions may be rationalized by the fact that Pd^0 formation is required for initiation of the catalytic cycle. Reduction of the metal in **10** or **13** seems unfavorable because of the strong donor ability of the dicarbene ligands and because of the rigid 85° bite angle, which favors a square planar geometry.

Given the high electron density at palladium, oxidative addition reactions may be more likely to be mediated by complexes such as **10**. Preliminary studies concentrated on the hydrogenation of

cyclooctene and indicated appreciable activity for the solvento complex **15** (Eq 2). Carbene C(4)-bonding seems to be essential for high catalytic activity, since the C(2)-bound analog **16** is a significantly less active hydrogenation catalyst (Figure 3).



(2)

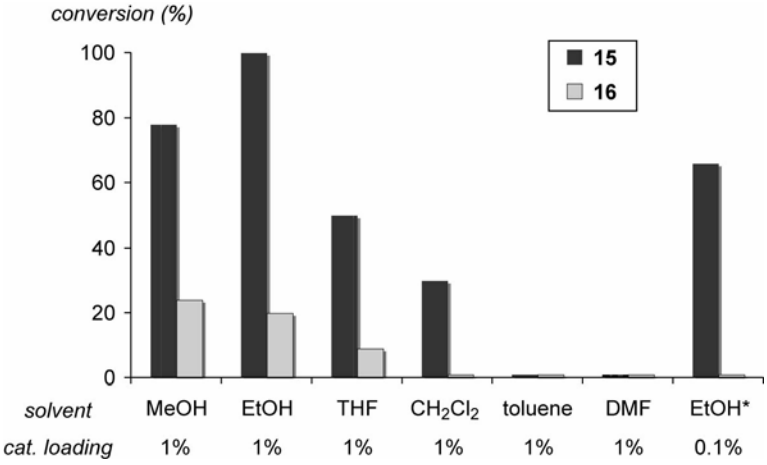


Figure 3. Hydrogenation of cyclooctene with the C(4)-bound dicarbene complex **15** and its normal analog **16** in different solvents. Conversions (GC) determined after 8h (* after 24h).

Hydrogenation reactions were typically run under mild conditions, that is, at room temperature and under atmospheric H_2 pressure. Conversions are fastest when using EtOH as solvent. Under these conditions hydrogenation of cyclooctene is complete in less than 5h, whereas in non-polar solvents like toluene the conversion is incomplete even after prolonged reaction times. Strongly coordinating solvents such as DMF appear to poison the catalytic activity of the complex and no conversion is observed at all.

Under the applied conditions, 1 mol% catalyst loading is required for useful conversions. At 0.1 mol% loading, cyclooctene reduction proceeds to about 70% and at even lower loadings (0.01

mol%) only traces of product were detected. Since hydrogenation is supposed to be initiated by oxidative addition of H_2 to the metal center, the high catalytic activity of **15** may be another consequence of the exceptional donor power of abnormally C(4)-bound carbenes.

Conclusions

Detailed analyses and reactivity studies have shown that C(4)-bound carbenes are exceptionally strong donor ligands that surpass C(2)-bound carbenes. This electronic impact has remarkable consequences on the stability and reactivity of the coordinated metal center. We have exploited these effects in catalytic alkene hydrogenation and have developed an efficient system based on abnormal carbene bonding. Similar complexes may become promising candidates for the activation of other less reactive bonds.

Acknowledgement

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